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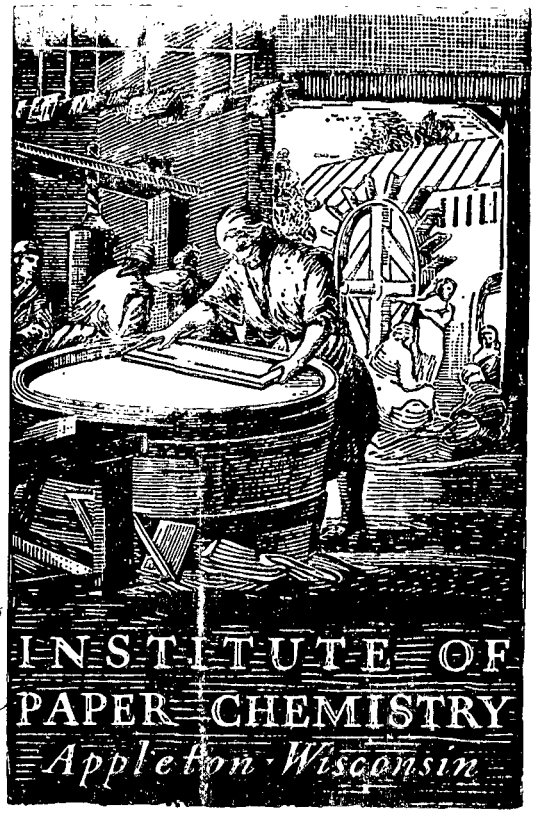

CAUSTIC STRESS CORROSION CRACKING OF CARBON STEELS

A Supplement to

STRESS CORROSION CRACKING OF CONTINUOUS DIGESTERS

Project 3589

Final Report

~~A~~ Progress Report

to

DIGESTER CRACKING RESEARCH COMMITTEE

October 17, 1986

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

CAUSTIC STRESS CORROSION CRACKING OF CARBON STEELS

A Supplement to

STRESS CORROSION CRACKING OF CONTINUOUS DIGESTERS

Project 3589

by

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Section Leader

Corrosion and Materials Engineering

Final Report

A Progress Report

to

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A Supplement to

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SUMMARY

This report supplements the final report to the Digester Cracking Research Committee on stress corrosion cracking of Kamyr continuous digesters.* It provides an introduction to stress corrosion cracking for those who are unfamiliar with the concepts and terminology of this topic. Included in the report are an introduction to caustic cracking, a summary of test methods used in the DCRC program to investigate stress corrosion cracking, and a glossary of terms.

R. Yeske, "Stress Corrosion Cracking of Continuous Digesters: A Summary of Digester Cracking Research Committee Projects," Final Report on Project 3589 (October, 1986), available from The Institute of Paper Chemistry, Appleton, WI.

AN INTRODUCTION TO CAUSTIC CRACKING*

Carbon steels are known to be susceptible to a form of stress corrosion cracking known as caustic cracking or caustic embrittlement. In caustic cracking, cracks initiate and grow along microstructural features called grain boundaries in the carbon steel. Extensive crack branching is also a distinguishing feature of caustic cracking (Fig. 1). The driving force for crack propagation is a high tensile stress applied externally to the steel and/or residing within the steel as a result of fabrication. There have been numerous incidents of caustic cracking failures reported in several different industries over the years.

As with other forms of stress corrosion cracking, caustic cracking will occur only when several conditions are satisfied. First, a high tensile stress must be present in the steel while it is exposed to the corrosive medium. Second, the material must be susceptible to stress corrosion cracking in caustic. (Nearly all carbon steels, including base metal and weld filler metal, are thought to be susceptible to caustic cracking.) Next, the corrosive environment must spontaneously react with the steel to form a film on the wetted surface that offers only limited corrosion protection to the underlying metal. Finally, the electrochemical potential (i.e., the voltage) spontaneously developed on the surface of the wetted steel must remain within a specific range. This voltage is thought to condition the surface film to allow crack initiation and growth. All of these conditions must be fulfilled at the same time in order for caustic cracking to proceed.

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*A detailed review of caustic cracking is available in an earlier report.[1]

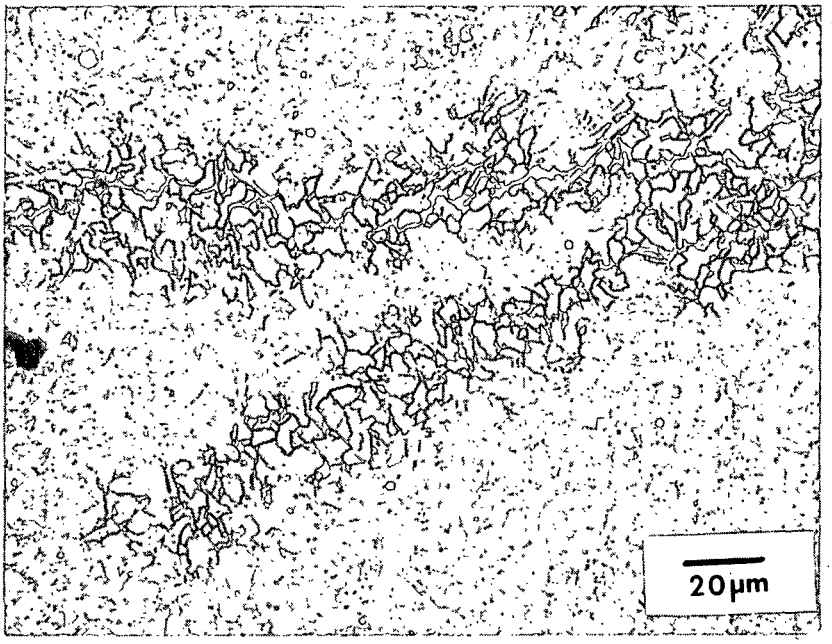


Figure 1. A photomicrograph showing caustic cracking along microstructural features in steel as revealed by metallographic etching.

Tensile stresses can arise in carbon steel pressure vessels from various sources. The principal source of stress in welds is the differential contraction that occurs as welds cool under restraint during vessel fabrication. If a stress relieving heat treatment is not performed on the steel after welding the residual stresses remaining at the weld are on the order of the tensile strength of the steel — as high as 60,000 pounds per square inch.[2] These residual stresses remain in the weld and the adjacent base metal unless they are relaxed by a stress relief heat treatment or by cracking. Operating stresses can also contribute to the driving force for crack growth, especially at discontinuities in the metal that can raise the effective local stress. In continuous digesters, as in all ASME Code vessels, the nominal stress arising from pressurization is on the order of one-fourth of the tensile strength of the steel, but the local stress can be much higher where surface imperfections,

scratches, and other defects concentrate the stress. Small fluctuations in stress — perhaps arising from pressure fluctuations during routine operation — are thought to increase the propensity for cracking.

All plain carbon steels used in fabrication of pressure vessels are thought to be susceptible to caustic cracking, including both base metals and weld filler metals.[1] This list of susceptible steels includes A516 Gr.70, A285 Gr.C, and A212 Gr.B pressure vessel steels, and E7018 and E6010 weld filler metals, all of which were used in the construction of Kamyr digesters. Stainless steels appear to be resistant to cracking in kraft cooking liquors at impregnation zone temperatures, although cracking can occur when the temperatures are higher, when the caustic concentrations are increased, or when the stainless steel microstructure is sensitized by an improper heat treatment.

Caustic cracking of carbon steel occurs over a wide range of caustic concentrations. The lower limit for cracking appears to be in the range of a few percent (by weight) of caustic as NaOH. In kraft cooking liquors, the concentration of hydroxides at the site of cracking is typically on the order of 3 to 5 percent,[3] which is sufficient to induce cracking of carbon steels if all other conditions for cracking are satisfied.

If caustic cracking is to proceed, the potential (i.e., the voltage) developed spontaneously at the wetted metal surface must remain in a critical range while the stress is being imposed. The range of potentials that will cause cracking depends on the caustic concentration[4], as shown in Fig. 2. Concentrated caustic solutions will induce caustic cracking of carbon steels over a wide potential range. As the concentration of NaOH decreases toward five percent (by weight), the width of the potential zone for caustic cracking

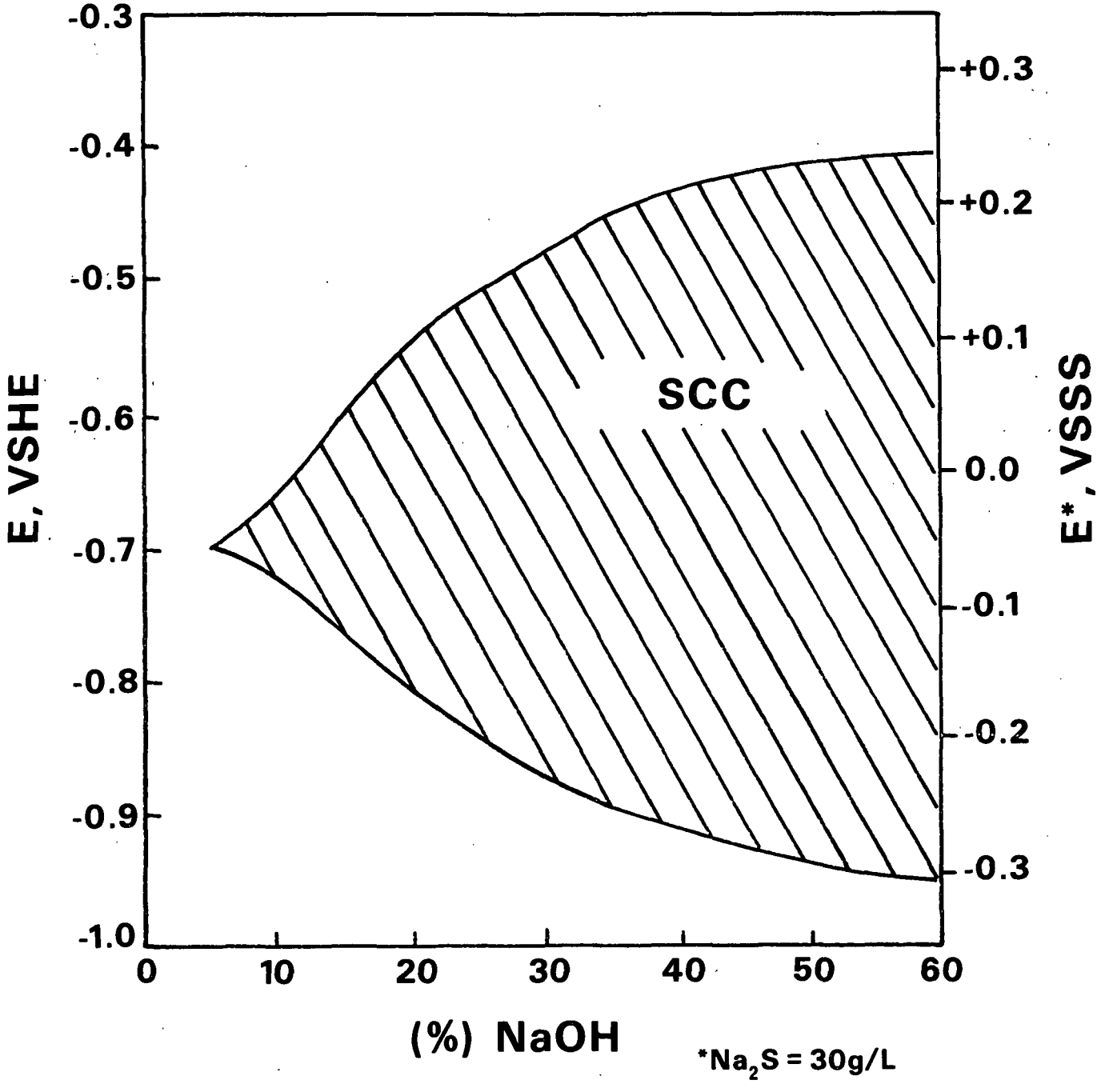


Figure 2. A schematic plot showing the potential range where caustic cracking can occur, as a function of the caustic concentration of the environment.[4]

decreases dramatically. Below a few percent of dissolved caustic, the potential range shrinks to zero and caustic cracking does not occur.

In general, the electrochemical potential measured at the surface of carbon steel wetted by kraft cooking liquors has been found to be close to the potential range associated with caustic cracking. However, the factors which determine this potential are not well understood.

The critical requirements for caustic cracking can be rationalized in terms of a generally accepted mechanism of crack growth (Fig. 3). This model for caustic cracking, often referred to as the slip-dissolution model, envisions crack growth as a series of repetitive dissolution events occurring at the tip of a growing crack. The film that forms on most of the wetted steel surface prevents active corrosion of most of the surface wetted by the caustic solution. However, tensile stresses that deform the steel slightly at the tip of the crack rupture the attached film at the crack tip. Once the protective film is destroyed, rapid corrosion occurs at the crack tip, resulting in apparent penetration of the crack. Eventually, the film reforms at the crack tip, only to be ruptured again by the tensile stresses and followed by another dissolution event. In this way, cracks grow by repeated film rupture and dissolution events that take place at the crack tip.

Caustic cracking will generally follow a preferred path through the steel microstructure as shown in Fig. 1. The reason for this preferred path of cracking remains controversial, but is probably associated with either unique electrochemical conditions or unique strain conditions that develop at the microstructural boundaries in the steel. These conditions exist because of the unique composition and structure associated with grain boundaries.

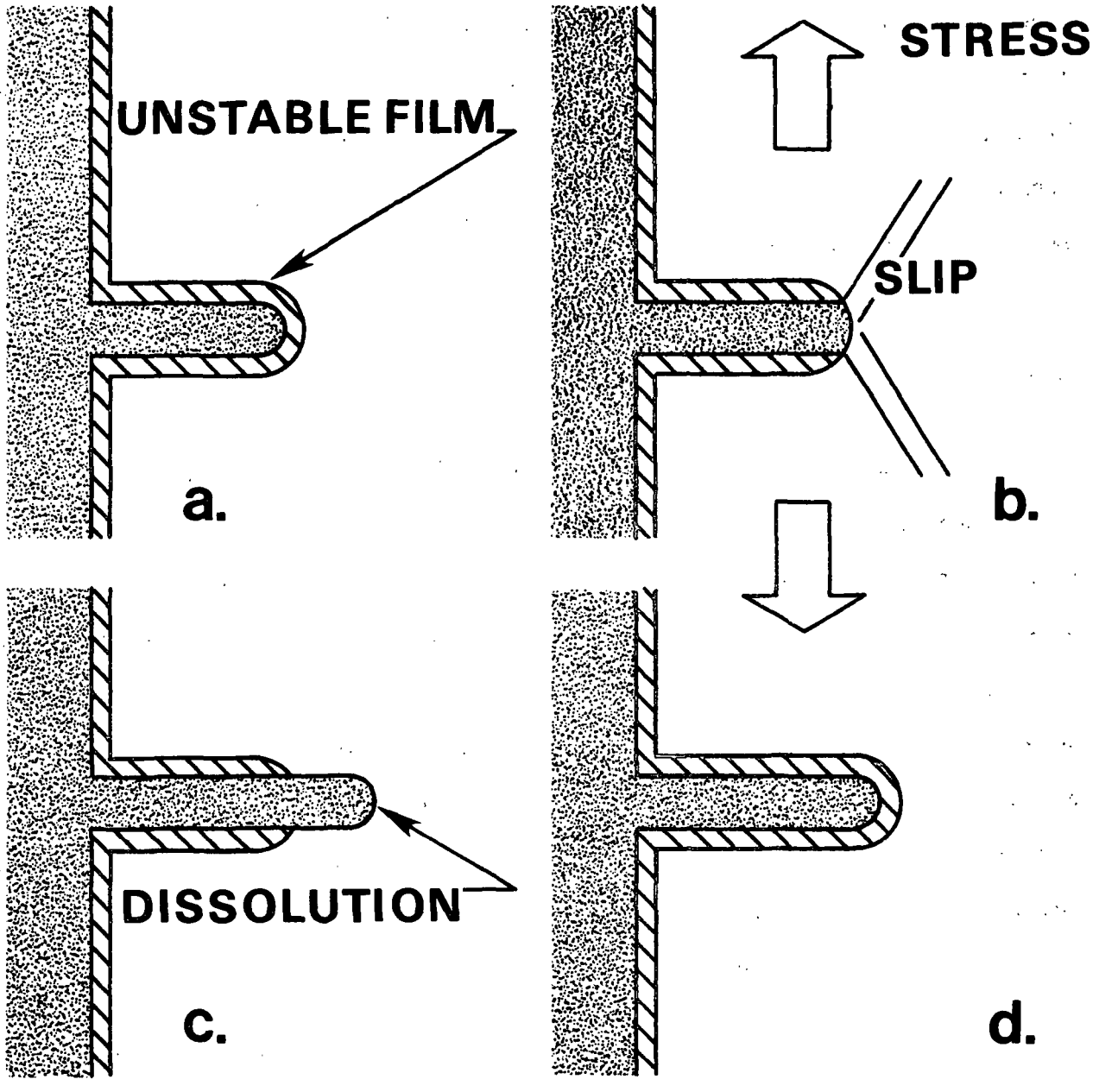


Figure 3. A schematic diagram showing the repetitive mechanism of caustic cracking as visualized in the slip-dissolution model.

ACCELERATED TEST METHODS

Several different accelerated test methods were used to investigate stress corrosion cracking in the DCRC programs.[5-12] Accelerated tests are necessary because the incubation time for cracking at welds exposed to cooking liquors can be quite long. Consequently, accelerated tests, such as the slow strain rate test (SSRT) and fracture mechanics testing for crack growth, were employed in many phases of the DCRC program. The objective of this brief subsection is to describe these accelerated tests.

CONTROLLED POTENTIAL TESTING

The potential difference (or voltage) found at the wetted metal surface is an important variable in stress corrosion cracking studies because it has such a strong effect on cracking susceptibility. Cracking does not occur unless the potential developed at the metal/electrolyte interface remains within a specific zone. To identify this cracking zone, tests must be conducted to determine the cracking susceptibility at various potentials. The zone where cracking is observed can then be compared with the potential that spontaneously develops at a wetted metal surface in the laboratory or in the field. This subsection addresses the origins of electrochemical potentials and briefly considers how potentials can be measured and controlled.

Every metal immersed in an electrolyte will spontaneously develop a voltage (or potential) at its wetted surface. In a lead-acid storage battery, for example, the voltage difference between the positive and negative terminals arises because plates of two different materials are immersed in the battery acid. A separate voltage develops at each of the plates but neither of these separate voltages can be easily measured. However, the voltage of the battery

can be easily measured as the algebraic difference between the potentials developed at each of the two plates. Pressure vessel steels immersed in kraft cooking liquors also develop their own characteristic potentials.

The potentials that exist on wetted metal surfaces are easily measured using a high-resistance DC voltmeter and a reference electrode, as shown in Fig. 4. One terminal from the voltmeter is connected to the metal and the other terminal (the low or common terminal) is connected to a reference electrode immersed in the same electrolyte. The voltmeter measures the algebraic difference between two voltages — the voltage at the metal surface and the voltage measured at the reference electrode surface. The reference electrode provides a stable, reproducible, well-known voltage as a benchmark against which other potentials can be measured. (In some respects, the reference potential for corrosion measurements resembles earth ground potential in electrical power measurements.) Whenever the potential of a metal is measured, the reference potential used in the measurement must also be specified.

Some common reference electrodes are the Saturated Calomel Electrode (SCE), the Standard Hydrogen Electrode (SHE), and the Silver/Silver-Sulfide electrode (SSSE). It is agreed that the SHE electrode is the universal reference electrode standard and the potential of this electrode is arbitrarily assigned a voltage of 0.000 V. The SHE electrode is not widely used because it is more difficult to use and maintain than alternative reference electrodes. The potential of the SCE reference electrode is about 241 millivolts above the SHE potential. The SSS reference electrode has a reference potential about 890 millivolts below the SHE potential in typical cooking liquor, but the exact potential of this electrode depends on the sulfide concentration.

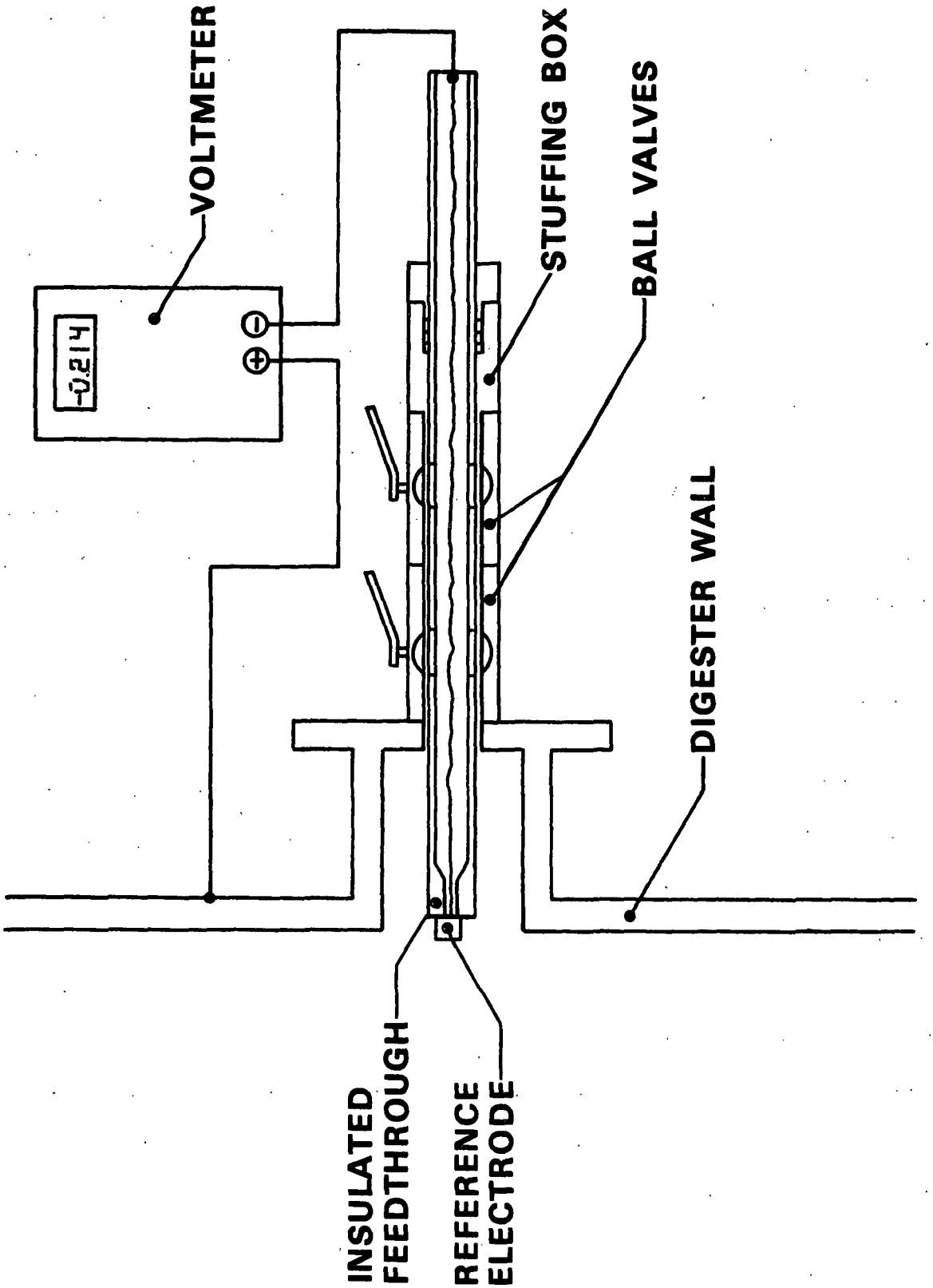


Figure 4. Measurement of the potential (or voltage) developed at a surface wetted by an electrolyte such as kraft cooking liquor.

The voltage of a metal measured with any reference electrode can be referred back to the universal standard (the SHE potential) by subtracting (algebraic subtraction) the reference potential of the reference electrode from the voltage measured at the voltmeter. For example, a steel immersed in cooking liquor may have a measured potential of -1000 mVSCE, which means that the potential of the steel/liquor interface is one thousand millivolts below the standard potential established at a Calomel reference electrode. But the Calomel reference potential is 241 mV above the SHE potential. The same steel would have a potential of -759 mVSHE [i.e., -1000 - (-241) = -759 mV] if the Standard Hydrogen Electrode was used as the reference electrode.

The potential that spontaneously occurs at wetted metal surfaces is called the rest potential (or open circuit potential) and is often given the symbol, E_{corr}. As with all corrosion potentials, E_{corr} must be referred to a specific reference electrode potential. E_{corr} is established by a complex interaction between the wetted metal and the contacting electrolyte. The E_{corr} of a material exposed to an electrolyte may vary with time, depending on changing conditions at the wetted surface.

The potential at a metal surface may be artificially shifted from the rest potential in two ways — by connecting the metal to a DC power supply or by adding oxidizing or reducing species to the electrolyte. The shift in potential from E_{corr} is called a polarization. E_{corr} can be increased relative to the usual rest potential by doping the electrolyte with oxidants — species that will readily consume electrons at the metal surface. The potential can also be increased above E_{corr} by connecting the metal to a battery whose polarity and voltage make it a sink for electrons. Potentials below E_{corr} can be achieved by

adding reducing species to the environment or by connecting the metal to a battery acting as a source of electrons. In most instances, it is more convenient to change potentials with a DC power supply.

When a power supply is used to control potentials, it will act as either a sink or a source of electrons for the metal electrode; an electrical current will flow from (or to) the power supply as the potential is shifted from the rest potential. This current must flow through the wetted metal surface, through the electrolyte, and back to the power supply through another metal immersed in the electrolyte (Fig. 5). This second metal electrode, often called the counter electrode, is connected to the second terminal of the power supply when potentials are being shifted. The counter electrode is only needed when the potential of a metal is artificially shifted from the rest potential by connection to a battery or other DC power source. The current required to shift the potential can be measured by an ammeter connected between the power supply and the counter electrode.

A special DC power supply used to polarize metals in corrosion tests is called a potentiostat. When controlled potential tests are performed, the test specimen and the other required electrodes are connected to a potentiostat as shown in Fig. 5. The desired potential is set by adjusting the set-point control on the potentiostat. The potentiostat passes current of appropriate polarity and magnitude to hold the desired potential throughout the test.

The rest potential, E_{corr}, measured at the surface of a steel surface exposed to caustic cooking liquors is an important quantity since E_{corr} can lie within the range required for cracking. The potentials measured during polarization of a steel electrode, and the current required to achieve those potentials

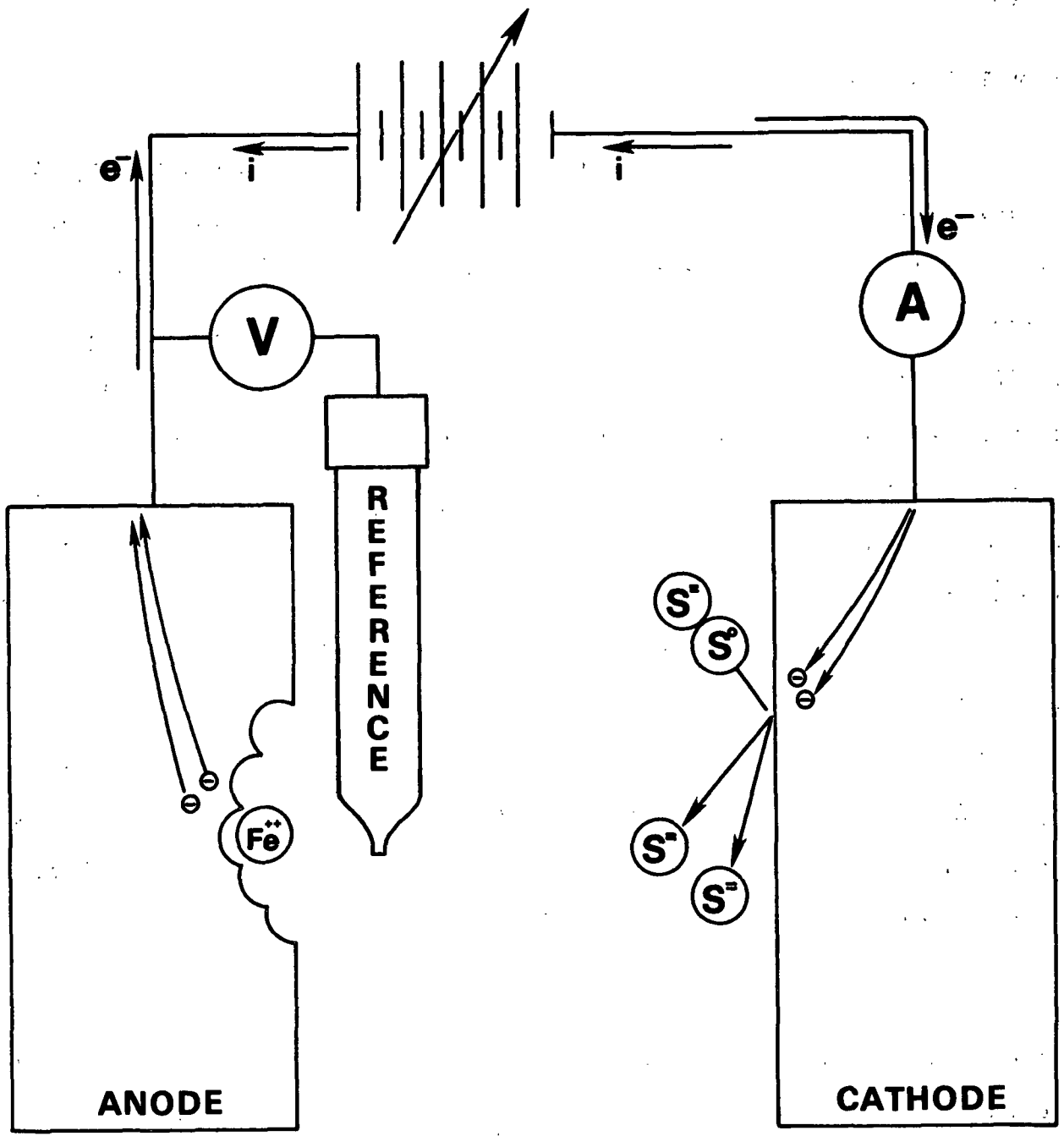


Figure 5. Schematic diagram of the electrical current flow associated with a polarization of a metal to potentials above E_{corr}, i.e., an anodic polarization.

describe the electrochemical behavior of the steel in the cooking liquor, as follows.

POLARIZATION CURVES

A polarization curve is a semilogarithmic plot of potential versus log (applied current) data obtained when the potential is systematically scanned from E_{corr} in a positive or negative direction. Polarization curves are determined by programming a potentiostat to scan potentials while the log (applied current) is recorded. The potential is controlled and measured as described above. The current is the current provided by the DC power supply to achieve a given potential, and is measured by an ammeter connected between the power supply and the counter electrode as shown in Fig. 5. The applied current is usually normalized by dividing the current by the exposed surface area of the electrode to obtain a current density, in units of amps/sq. cm. An anodic polarization curve shows polarizations to potentials higher than the rest potential, while cathodic polarizations achieve potentials below the spontaneous E_{corr} value. Anodic polarizations generally increase the rate of metal dissolution, while cathodic polarizations decrease dissolution rates, although there are exceptions as described below.

Polarization curves, particularly anodic polarization curves, provide considerable insight into the electrochemical behavior of a metal immersed in an electrolyte. Three types of behavior are encountered when anodic polarization curves are generated, as shown in Fig. 6. An active metal is characterized by an increasing applied current as the potential is increased. This behavior is typical of metals that corrode actively without the formation of protective films. Steel immersed in hydrochloric acid solutions will experience active

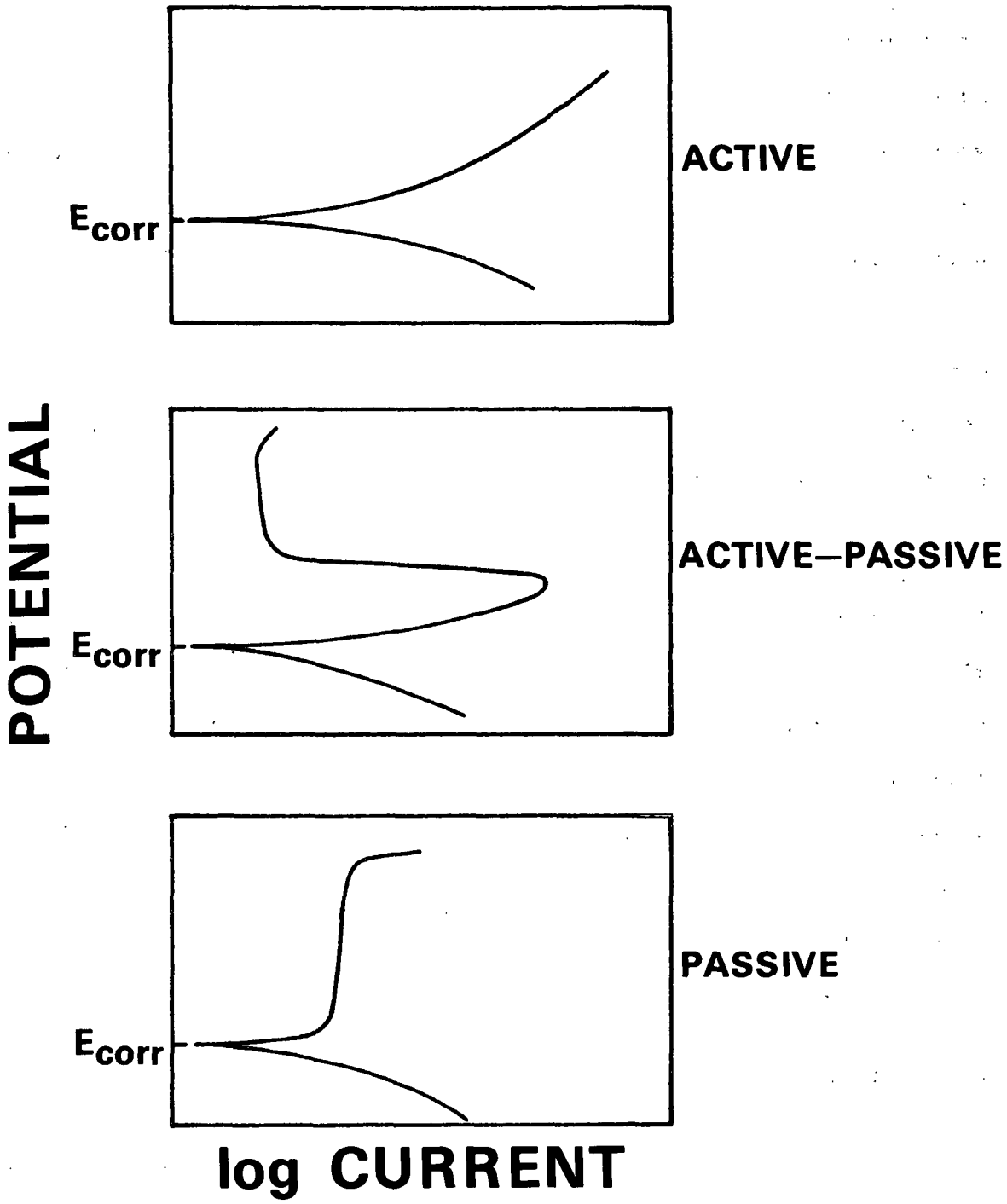


Figure 6. Three types of electrochemical behavior as represented by anodic polarization curves, (a) active, (b) active-passive, (c) passive.

corrosion. Passive metals are protected by surface films and show little increase in dissolution current with increased potential. Stainless steels are examples of materials made passive by the presence of a chromium-rich surface film that protects the underlying metal. Active/passive behavior occurs when a metal initially exhibits active corrosion behavior but reverts to passive behavior once the potential is raised above a certain threshold level called the active/passive transition potential. The onset of passivity in active-passive metals is associated with formation of a film on the surface of a metal which protects the underlying metal from corrosion. The film also reduces the applied current required to achieve higher potentials, which is a characteristic of passive behavior.

Active/passive behavior is important from a caustic cracking viewpoint because cracking is frequently observed at potentials where there is a transition from active to passive behavior (Fig. 7). The film that forms at the transition from active to passive behavior forms slowly and does not provide the level of protection to the underlying metal provided by passive films formed at somewhat higher potentials. As discussed earlier, films with poor integrity promote cracking by the slip/dissolution mechanism. Therefore, metals which undergo active/passive transitions are candidates for stress corrosion cracking when their rest potentials are in the active/passive range.

FAST-SLOW POLARIZATION AS AN ACCELERATED SCC TEST

Since polarization curves depict the film-forming characteristics of a corroding metal, polarization curves are often used to predict SCC behavior. As discussed above, an active-passive transition is a good indicator of SCC susceptibility, but it is often difficult to assign limits to the potential range associated with cracking in this active-passive zone.

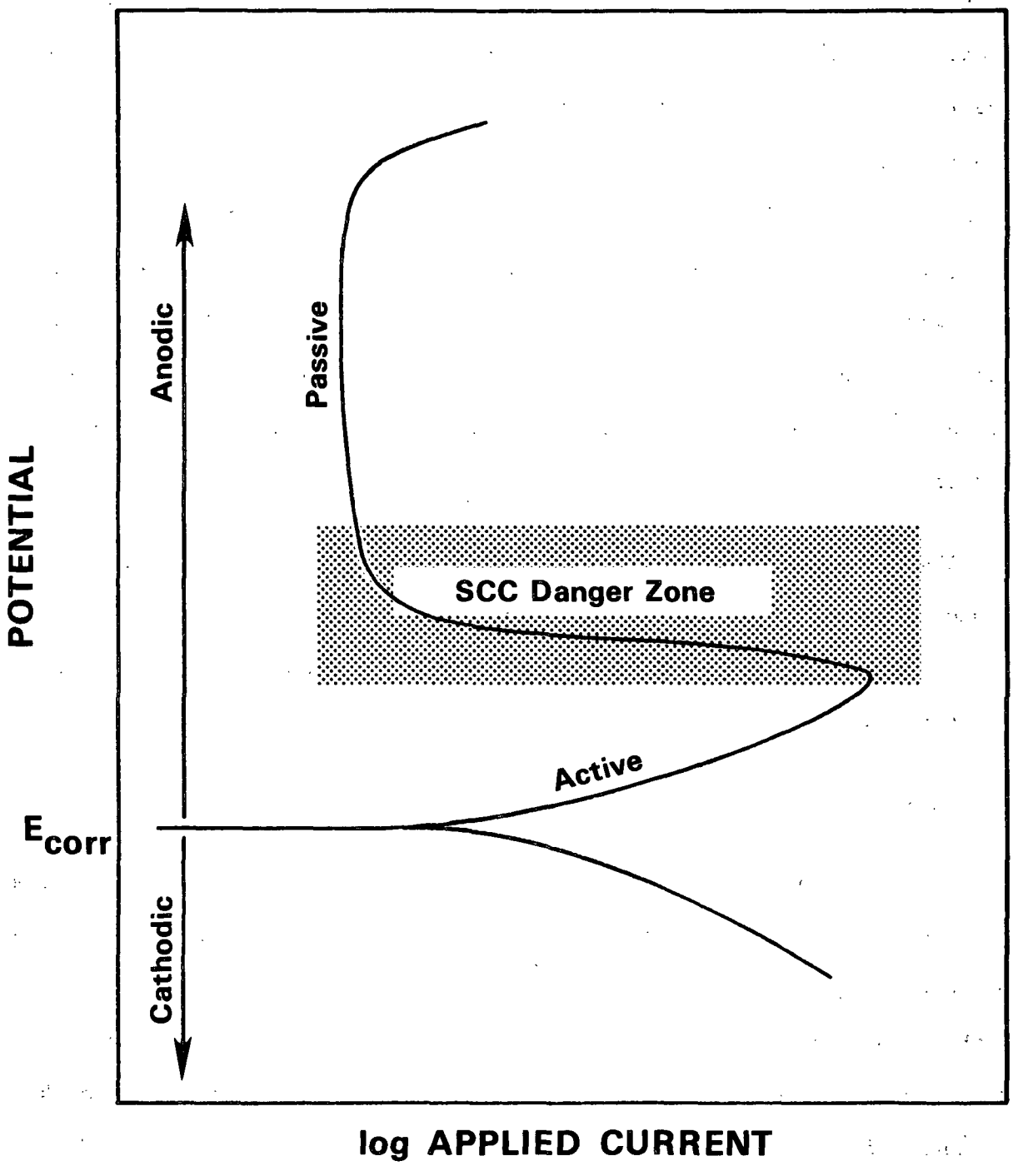


Figure 7. Typical cracking range for metals with active-passive corrosion behavior, as with carbon steels exposed to kraft liquors.

The fast-slow scan technique is an attempt to bracket the potential range for cracking with greater precision than can be achieved with a single polarization curve.[4] In this approach, the metal is subjected to two separate polarization scans, one fast and one much slower, and the polarization curves from the two scans are compared as shown in Fig. 8. Although rapid scanning through anodic potentials usually requires a slightly higher current at the same potential, the differences between the fast and slow scan curves are generally small. However, large differences in the current density during fast and slow scans sometimes indicate the range of potentials where cracking occurs. This difference between fast and slow scan curves can be used to show the potential range where cracking is likely to occur.

Thus, fast and slow scan polarization curves generated on pressure vessel steels immersed in cooking liquors might be exploited as an accelerated test to identify the potential range for cracking. This approach was examined in the PPRIC program.

SLOW STRAIN RATE TESTING

One of the accelerated tests used in both the PPRIC and Battelle studies was the slow strain rate test (SSRT). This test has been found to be very useful for characterizing SCC susceptibility in a number of circumstances. With the SSRT method, specimens of the metal of interest are slowly strained while immersed in an environment that might induce stress corrosion cracking. Cracking susceptibility is determined by comparing the results of the slow tensile tests in air or other inert environment with those derived from a slow tensile test in a potentially aggressive environment. In some cases, a small cyclic load is superimposed on the slowly increasing tensile load to promote cracking.

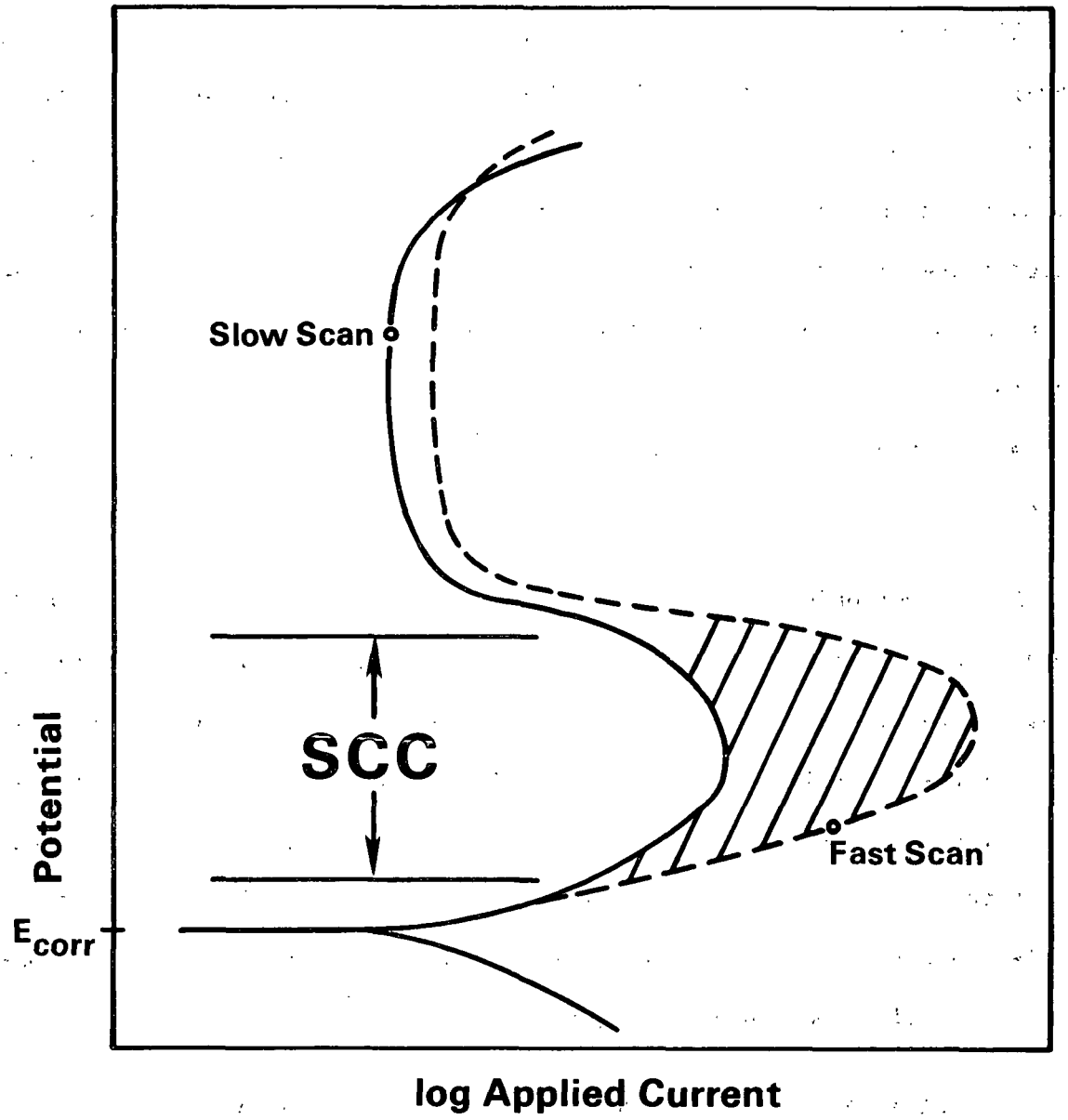


Figure 8. Schematic diagram showing the potential zone associated with cracking as revealed by the fast/slow scan technique.

In all cases, the specimens are strained to failure and cracking susceptibility is assessed by comparing the stress-strain curves and examining the physical appearance of failed test specimens.

If the environment causes stress corrosion cracking of the metal, the SCC susceptibility will be revealed by differences in behavior of specimens tested in inert and crack-promoting environments. The effects of stress corrosion cracking on mechanical properties are shown schematically in the load-elongation curves for tensile tests with and without cracking, in Fig. 9. When stress corrosion cracking occurs during the SSRT test, the total elongation of the test specimen at the point of final rupture is much reduced, since cracks initiate and grow early in the test, severing the specimen before normal elongations can develop.

Stress corrosion cracking susceptibility may also be revealed in a SSRT test by a reduction in the extent of necking of the gage section of the tensile specimen. In tensile tests without SCC, extensive necking usually occurs and there is a large reduction in the cross-sectional area of the specimen at the point of failure. If stress corrosion cracking occurs, failure occurs by crack growth before extensive necking can develop. One measure of the degree of necking is the percent reduction in cross-sectional area (RA) of the gage section of the tensile specimen at the point of fracture

$$RA = 100 \times (\text{Initial Area} - \text{Final Area})/\text{Initial Area}$$

Tensile tests without SCC are marked by extensive necking and a large RA, whereas tests conducted under stress corrosion cracking conditions will have a smaller RA.

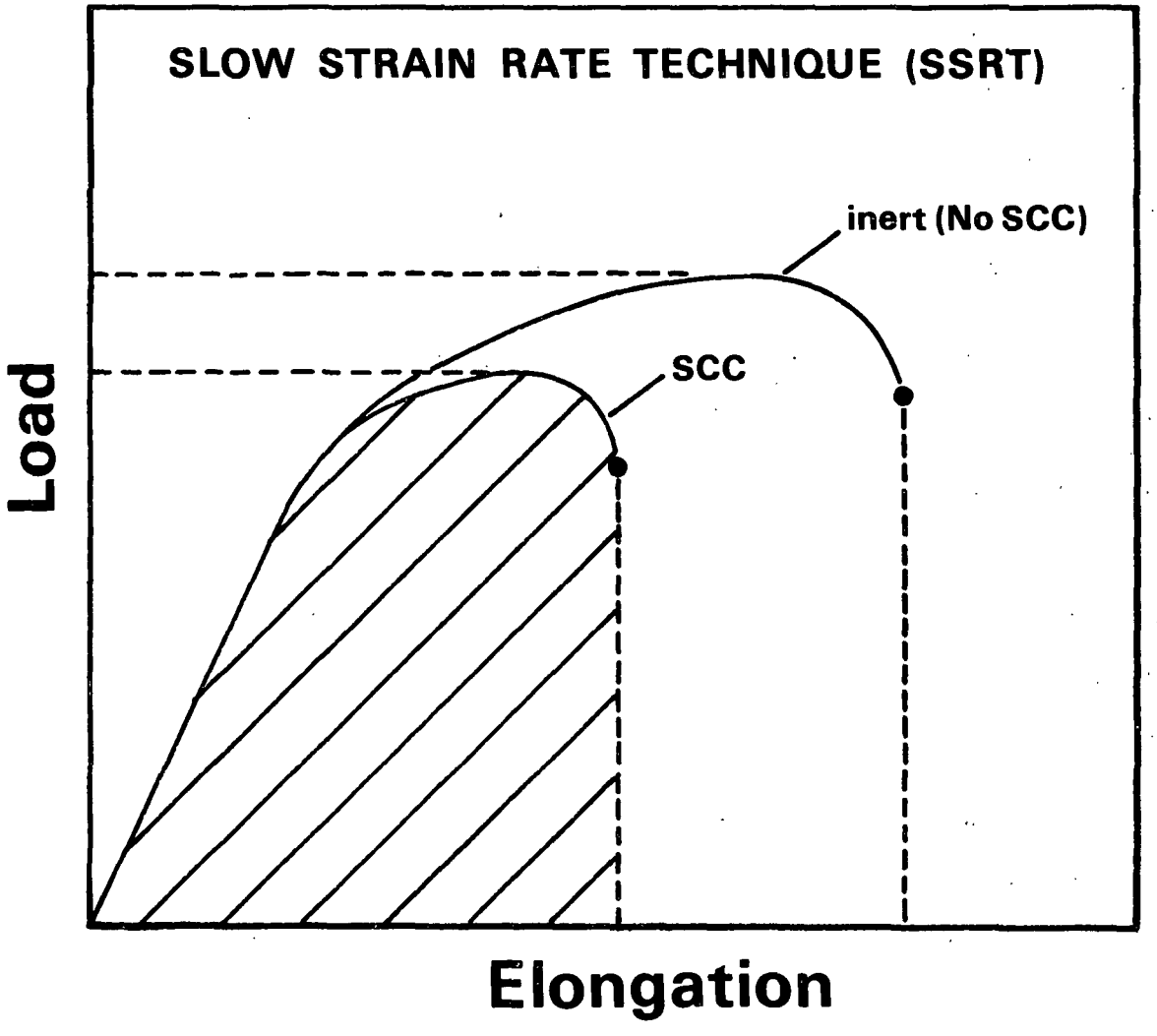


Figure 9. A schematic example of the load-elongation curves for SSRT tensile tests in crack-promoting and inert environments.

Another indicator of cracking susceptibility is a loss of tensile strength — the maximum load applied during the tensile test divided by the original cross-sectional area of the gage section. SCC can be detected in SSRT testing by a diminished tensile strength compared to the normal tensile strength developed during a SSRT test in air or other inert environment.

A final indicator of stress corrosion cracking susceptibility is the formation of many small cracks on the surface of the gage section close to the point of rupture. These secondary cracks are normally absent from tests in inert environments that do not cause stress corrosion cracking, but appear when the environment induces cracking.

The most sensitive measure of SCC susceptibility in an SSRT test is the appearance of secondary cracks on the gage section in the vicinity of the point of failure. Loss of elongation and reduction in area are also fairly sensitive indicators of SCC susceptibility in the SSRT test. Loss of strength is relatively insensitive as an indicator of SCC susceptibility, as extensive secondary cracking must occur soon after the start of the SSRT test for significant effects on tensile strength to become apparent.

SSRT tests are particularly useful to determine the range of potentials where cracking is possible. An artificial potential can be imposed on the test specimen during the slow strain rate tests to assess SCC susceptibility at that potential. SSRT tests conducted at several different potentials will establish the range of potentials where SCC is expected. Rest potential measurements will then indicate whether stress corrosion cracking will occur during exposure without polarization. The SSRT test data also indicate the minimum potential that must be achieved to prevent cracking by anodic protection. This approach was used extensively by PPRIC in their studies of digester cracking conditions.

The SSRT test is effective as an accelerated SCC test method because the slow deformation imposed on the test specimen is similar to the slow deformation process thought to occur at the crack tip during caustic cracking. The slow stretching of the test specimen ruptures the protective film on the metal surface and promotes the localized dissolution processes that are responsible for crack growth. Many cracks initiate and grow at the ruptured film sites, leading to a multitude of secondary cracks and corresponding losses of strength and ductility.

The SSRT test is recognized as a fairly severe test of the SCC resistance. SSRT testing is useful to screen for conditions that COULD cause cracking, but such cracking may not occur, or may not be as severe, under actual service conditions.

CRACK GROWTH RATE TESTING

The rate of crack growth under severe static loading conditions is another good indicator of the stress corrosion cracking susceptibility of a metal exposed to an aggressive environment. Crack growth rates are usually measured using precracked specimens that are preloaded in a controlled fashion and then exposed to the environment for a period of time. The average rate of crack growth is determined by measuring the difference in crack length before and after exposure and dividing by the exposure time to obtain the average crack velocity.

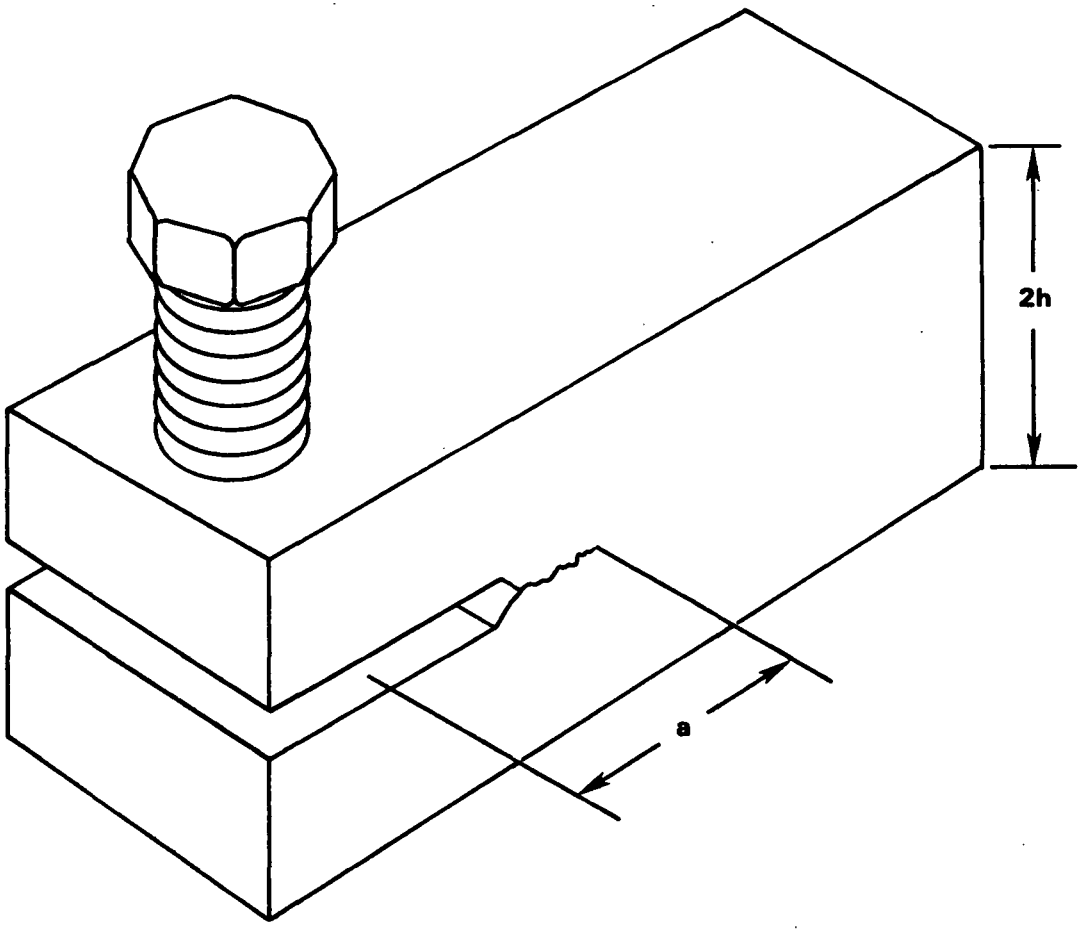
The driving force for crack growth obviously depends on the stress applied to the specimen during the exposure, but also depends on the length of the crack and the geometry of the test specimen. All of these factors which

influence crack growth rates are included in a quantity called the stress intensity, K, which is a measure of the driving force for crack propagation. Laboratory tests to determine crack growth velocities are usually conducted on specimens whose stress intensities can be calculated according to published formulas.

The double cantilever beam (DCB) specimen shown in Fig. 10 is commonly used for crack growth studies; it was used extensively by PPRIC in their DCRC research projects. The DCB specimen is mechanically precracked before exposure to the test solution to provide a sharp crack tip where further cracking will be easily induced. The specimen is loaded by forcing the crack faces apart in controlled fashion. Usually, a wedge is forced into the notch of the DCB specimen or a bolt is torqued to spread the notch faces apart. The distance separating the crack faces along the line of loading is called the crack opening displacement, V. The stress intensity for a DCB specimen is given in Fig. 10 as a function of the crack opening displacement, crack length, and geometry of the specimen. As cracks grow in the bolt-loaded DCB specimen, the crack length increases but the load is relaxed even more quickly; consequently, the stress intensity rapidly decreases as the crack length increases during a typical crack growth test (see inset, Fig. 10).

The crack velocity depends on the stress intensity in a complicated way, as shown schematically in Fig. 11. Note that the crack velocity is plotted on a logarithmic scale to accommodate the large changes in crack velocity that are usually observed. When the applied stress intensity is low — because the applied loads are small or the crack is short — the crack velocity is strongly dependent on the stress intensity. In this region, small increases in stress intensity result in large increases in crack velocity. At somewhat higher

DOUBLE CANTILEVER BEAM SPECIMEN



$$k_I = \frac{VEh\,(3h\,(a + 0.6h)^2 + h^3)^{1/2}}{4\,((a + 0.6h)^3 + h^2 a)}$$

E = Young's Modulus

h = Half Height

a = Crack Length

V = Crack Opening Displacement

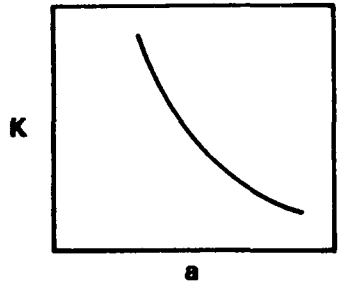


Figure 10. The Double Cantilever Beam (DCB) specimen with a formula for stress intensity as a function of crack opening, crack length, and specimen geometry.

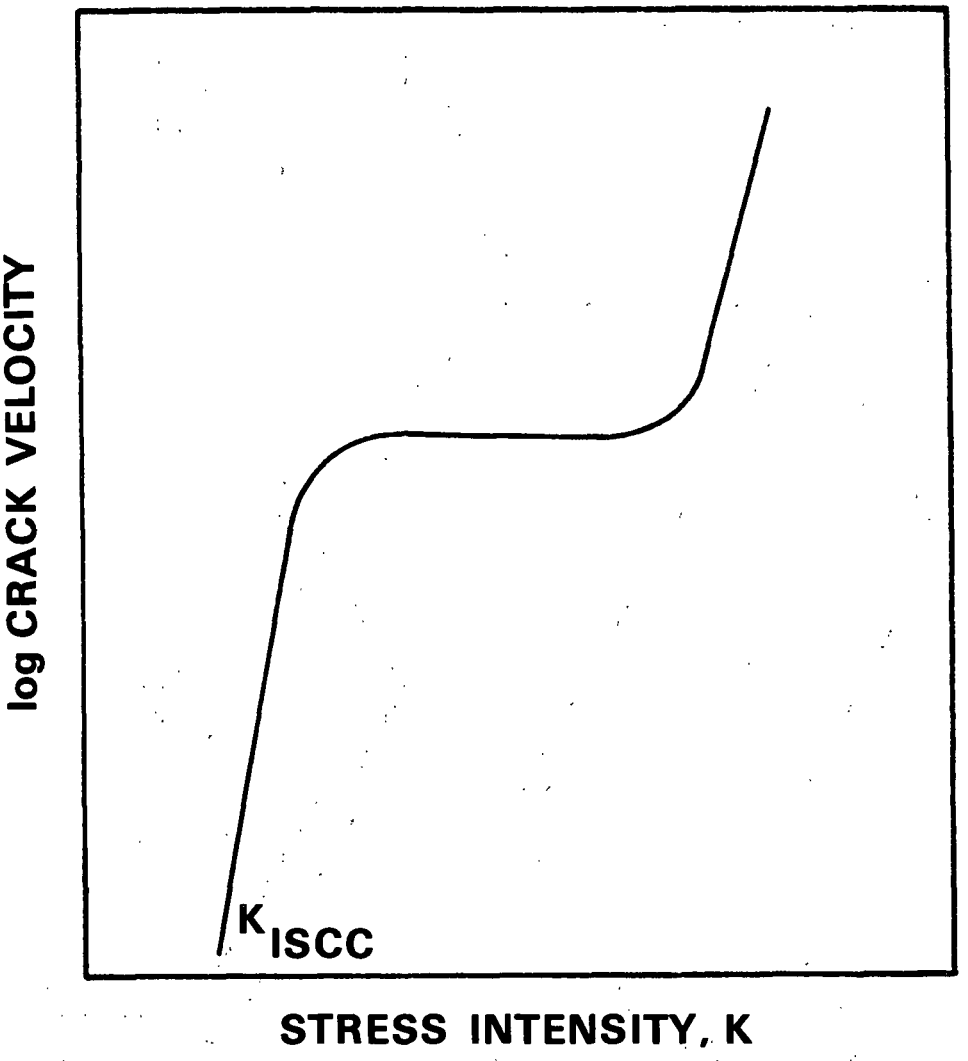


Figure 11. Schematic diagram showing the typical dependence of crack velocity on stress intensity.

stress intensities, crack velocity becomes independent of stress intensity. In this zone, commonly referred to as the plateau region, the velocity of cracking is fairly constant over a wide range of stress intensities and crack growth appears to be controlled by the rate of diffusion of aggressive species down the length of the crack. At still higher stress intensities, crack velocities increase once again because of mechanical overload effects.

Below a critical stress intensity level, no crack growth is observed. The stress intensity marking the transition from the no-crack to crack-growth regimes is called the threshold stress intensity, $K_{I_{scc}}$. If the stress intensity lies below $K_{I_{scc}}$ because the crack length is short or because the applied stress is low, cracks will not propagate. Threshold stress intensities are usually determined by allowing crack growth to occur in DCB specimens (at steadily decreasing stress intensities) until no further growth is detected; the stress intensity where crack growth ceases is $K_{I_{scc}}$.

Crack growth rate testing using DCB specimens can also be done under controlled potential conditions to map the effect of potential on crack velocity. In this case, the DCB specimen is connected to a potentiostat to control the potential during the crack growth exposure.

The crack velocities measured in the laboratory can be used to estimate the crack velocity expected in actual service equipment, provided appropriate caution is exercised. Stress intensities can be assigned to cracked components in operating equipment such as digesters, provided the potential, geometry of the crack, and the magnitude of the stress is known (including all residual stresses). The velocity of crack growth expected in service situations can then be estimated by consulting the laboratory data relating crack velocity to

applied stress intensity. However, care must be taken to ensure that the conditions are the same in both the laboratory and field circumstances, since the master curves for crack velocity will depend on variables such as potential, solution composition, and metallurgical structure, to name a few.

CIRCULAR PATCH TEST SPECIMEN

The circular patch test specimen, sometimes called the ring weld coupon, is designed to retain the high tensile residual stresses that are present in a plate when it is welded under constraint. The specimen was originally designed for studies of cold cracking of welds but has since found use as a specimen for studies of stress corrosion cracking in weldments.[13-14] The circular patch test specimen was used by PAPRICAN in its investigation of the effectiveness of surface treatments to prevent caustic cracking of welds.[12]

The test specimen is prepared by placing deep multipass welds of circular shape on both sides of a thick plate which is constrained against movement during the welding process. Typically, constraint is provided by temporarily welding the plate to the welding table while the ring welds are made. The geometry of the specimen is shown schematically in cross-section in Fig. 12. Tensile residual stresses as high as 70 ksi were measured in the weld metal of circular patch test specimens. The heat-affected zone in the base metal near the weld exhibited tensile residual stresses on the order of 50 ksi. These residual stresses are similar to those expected (and measured) in continuous digester welds.[12]

The circular patch test specimen is a self-stressed test specimen suitable for studies of caustic stress corrosion cracking. In the PAPRICAN studies, the circular patch specimens were exposed to simulated cooking liquors

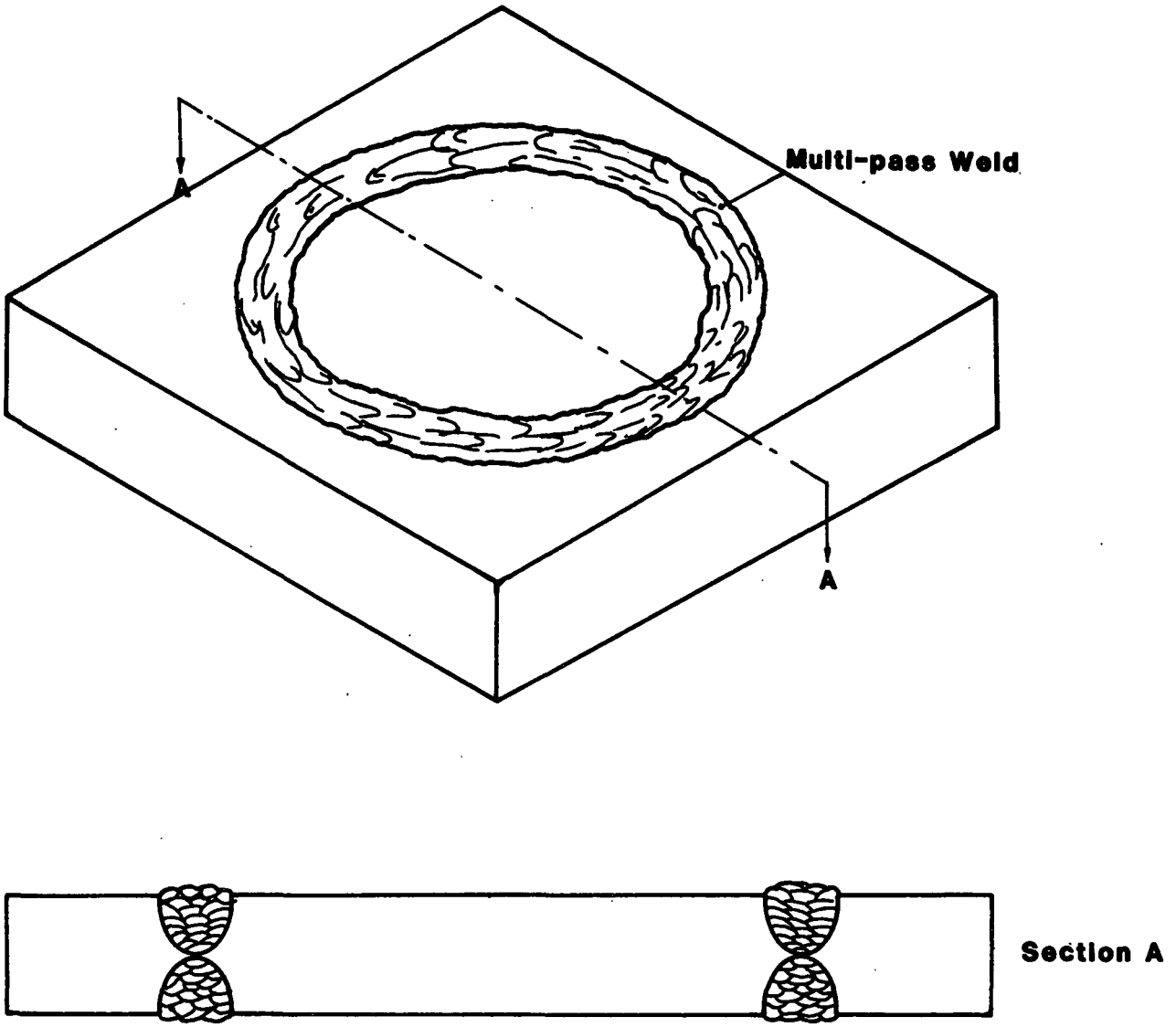


Figure 12. Schematic diagram of the circular patch test specimen.

at potentials chosen to induce cracking. Rapid stress corrosion cracking was observed on control specimens exposed in the as-welded condition. Some repair methods applied to other specimens were effective in preventing cracking.

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GLOSSARY

This is a glossary of terms used in connection with stress corrosion cracking.

Active - Term applied to a metal that is experiencing active corrosion, i.e., dissolution unimpeded by the presence of a protective, passivating surface film.

Anode - An electrode in an electrochemical cell where positive current enters the electrolyte and oxidation (e.g., dissolution) occurs releasing electrons.

Anodic Polarization - A shift in the electrochemical potential to potentials higher than the spontaneous rest potential.

Anodic Protection - An electrochemical technique to prevent corrosion or corrosion-assisted cracking of a metal by artificially raising its potential. Potential shifts are achieved using a DC power supply to pass electrical current through the wetted surface of the anodically protected metal.

Carbon Steel - A steel containing less than 2% carbon and only residual quantities of other elements, except those added for deoxidation (e.g., Si and Mn).

Cathodic Polarization - A shift in the electrochemical potential to potentials lower than the spontaneous rest potential.

Cathode - An electrode in an electrochemical cell where reduction occurs (consuming electrons) and positive current passes from the electrolyte into the electrode. In anodic protection, a cathode is installed to allow passage of current between the anodically protected structure and the DC power supply.

Caustic Cracking - A form of stress corrosion cracking that occurs in carbon steel exposed to hot caustic environments while simultaneously subjected to high tensile stress; also called caustic embrittlement.

Current Density - An electric current passing through an electrode in an electrochemical cell, divided by the surface area of the electrode; typical units are mA/cm^2.

DCB Specimen - A Double Cantilever Beam specimen is a test specimen that is used for measurement of crack growth rates. The specimen is precracked and then prestressed to promote crack growth during exposure to an appropriate environment.

E_{corr} - The rest potential that is spontaneously achieved when a metal is immersed in an electrolyte.

Electrode - A metal immersed in an electrolyte and participating in an electrochemical cell.

Galvanic Corrosion - Corrosion occurring as a result of electrical contact between dissimilar metals wetted by a common electrolyte.

Grains - Individual crystals which make up a polycrystalline material.

Grain Boundary - The interface between adjacent grains in a metallurgical structure.

Heat-Affected Zone - The area adjacent to a weld where the microstructure of the base metal has been altered by the heat applied during welding.

Intergranular Cracking - Cracking that occurs between grain boundaries or other interfaces in a metallurgical structure.

Open Circuit Potential - See rest potential.

Passive - The state of a metal surface covered by a surface film that substantially slows the rate of corrosion of the metal substrate.

Passivation - The formation of a protective surface film that substantially slows corrosion rates.

Polarization - The change in electrode potential caused by passage of current.

Potential - An electromotive force or voltage; the potential difference between a metal immersed in an electrolyte and the electrolyte adjacent to the wetted interface.

Reference Electrode - An electrode which exhibits a stable, reproducible potential that can be used as a voltage benchmark for the measurement of metal potentials.

Rest Potential - The potential that is spontaneously achieved when a metal is immersed in an electrolyte, E_{corr}.

Saturated Calomel Electrode (SCE) - A reference electrode whose reference potential is 241 mV above the SHE potential.

Standard Hydrogen Electrode (SHE) - A reference electrode whose potential is defined to be 0.000 volts and which constitutes the univeral reference potential standard.

Stress Corrosion Cracking - A form of corrosion-assisted cracking of metals induced by the presence of a static tensile stress during exposure of a susceptible metal to an appropriate electrolyte.

Stress Intensity - The mechanical driving force for crack growth, expresses as a product of terms involving applied stress, crack length, and crack geometry.

Threshold Stress Intensity - The stress intensity below which stress corrosion cracks will not propagate; $K_{I_{scc}}$.